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**THERMAL EFFECTS IN EQUILIBRIUM  
SURFACE SEGREGATION IN  
A COPPER - 10-ATOMIC-PERCENT-ALUMINUM  
ALLOY USING AUGER ELECTRON SPECTROSCOPY**

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16. Abstract  <p>Equilibrium surface segregation of aluminum in a copper - 10-atomic-percent-aluminum single-crystal alloy oriented in the [111] direction has been demonstrated by using Auger electron spectroscopy. This crystal was in the solid solution range of composition. Equilibrium surface segregation was verified by observing that the aluminum surface concentration varied reversibly with temperature in the range 550 to 850 K. These results were curve fitted to McClean's expression for equilibrium grain boundary segregation and gave a retrieval energy of 5780 J/mole (1380 cal/mole) and a maximum "frozen in" surface coverage three times the bulk layer concentration. Analyses concerning the relative merits of sputtering calibration and the effects of evaporation are also included.</p>					
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The physical mechanisms for surface segregation in alloys are not understood very well. In references 3 and 4 Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED) were used to demonstrate equilibrium segregation (ref. 5) of aluminum in single-crystal copper-aluminum alloys. These studies, however, presented only plausible evidence for equilibrium segregation. The objective of this report is to give more definite proof for equilibrium surface segregation in alloys.

The following concepts are explored: (1) the reversibility of surface concentration with temperature; (2) the effect of sputtering on surface segregation; (3) a more accurate determination of surface concentration and retrieval energy; and (4) determination of the "freezing in" temperature (ref. 5) for segregation.

In this study AES is used to determine the change with temperature of aluminum surface concentration in a copper - 10-atomic-percent-aluminum solid solution. The alloy is a single crystal in which the (111) plane is examined. The resulting data are curve fitted to McClean's expression for equilibrium segregation (ref. 5) in order to determine surface concentration and retrieval energy more accurately. Evaluations of the relative merits of a sputtering calibration for determining surface concentration and the effects of evaporation are also included.

## APPARATUS

The apparatus used for these studies is shown in figure 1 and described in detail in reference 1. Crystals could be rotated to allow both AES, LEED analysis and ion bombardment cleaning of the crystal surface.

The AES and LEED systems used are standard commercial equipment. A block schematic diagram of the equipment is shown in figure 1. The vacuum system used consisted of a bakeable stainless steel chamber which was evacuated by sorption pumps, a sublimation pump, and a  $140 \times 10^3$ -cubic-centimeter-per-second (140 liter/sec) ion pump.

## EXPERIMENTAL PROCEDURE

The crystal used for this study was a copper-aluminum solid solution containing 10 atomic percent aluminum. The crystal was triple-zone refined and contained less than 10 parts per million impurities. The sample was oriented to within  $1^\circ$  of the [111] direction by Laue diffraction. The crystal was polished with 600 grit paper and then electropolished with orthophosphoric acid. The crystal was heated by passing a current through its supporting straps with a low-noise 100-ampere direct-current power supply.

Temperature was measured with a Chromel-Alumel thermocouple spot-welded to the back face of the crystal.

The copper-aluminum sample was outgassed at 873 K until the pressure was in the low  $10^{-10}$ -torr range. Following outgassing, the crystal was alternately heated at 873 K and sputtered with argon ions until the Auger spectrum no longer showed traces of oxygen, carbon, or sulfur contamination (ref. 3).

When the data were taken the crystal was first sputtered for 1 hour with argon ions at an energy of 700 electron volts and a current density of 5 microamperes per square centimeter. Following sputtering the crystal was heated at 793 K for 1/2 hour. An impurity Auger trace was then taken. Auger traces giving the dependence of the aluminum peak height on temperature were taken at various temperatures in the range 273° to 943 K following heating at each selected temperature for 30 minutes. Six Auger traces were taken at each temperature setting and averaged in order to minimize the effects of instrumental noise. The calibration point of 793 K was repeated five separate times and represents an average of five independent measurements.

The current used to heat the crystal was found to interact with the collected secondary emission current. In order to establish that the observed decrease in aluminum Auger peak height (fig. 2) was a physical effect and not a current effect, the ratio of the two low-energy copper Auger peaks was taken over the whole current range. It was found to be constant. The aluminum peak height which is close to the copper peaks (within ~5 V) was normalized by dividing the height of the aluminum peak by the peak-to-peak height of the higher energy copper peak.

Improvements in the Auger equipment over reference 3 provided much smaller experimental spread in the data than was obtained in those cases.

In order to establish that the observed decreases in aluminum peak height with temperature were not a result of evaporation, a sheet of tantalum that was sputter cleaned was placed approximately 1 millimeter in front of the crystal. The tantalum was placed there for 17 hours at several crystal temperatures ( $>773$  K), after which the tantalum was examined for deposition of aluminum by taking Auger traces.

Typical experimental settings were an electron beam energy of 1500 electron volts, a modulation voltage of 2 volts peak-to-peak, a 300-millisecond time constant on the lock-in amplifier, and a sweep rate of 1.5 volts per minute on the retarding grids.

## ANALYSIS OF RESULTS

### Surface Concentration

McClean's (ref. 5) basic equation relating surface or grain boundary concentration to bulk concentration is given by

$$C_d = \frac{C_o \exp\left(\frac{Q}{RT}\right)}{1 - C_o + C_o \exp\left(\frac{Q}{RT}\right)} \quad (1)$$

where

$C_d$  fractional surface concentration of solute

$C_o$  fractional bulk concentration of solute

$Q$  retrieval energy

$R$  , gas constant, J/(mole)(K); cal/(mole)(K)

$T$  , temperature

In order to determine  $Q$  and obtain the surface coverage, the raw data were treated as follows. The measured Auger peak height ratio at a temperature  $T$  was divided by the peak height ratio at 793 K and equated to the following expression:

$$A(T, Q, C_o, C_1) = \frac{C_d(T) + C_1}{C_d(793 \text{ K}) + C_1} \quad (2)$$

where  $C_1$  is the sum of concentrations added for the number of layers assumed sampled by the Auger beam below the aluminum surface layer. Auger spectroscopy is sensitive to the total number of atoms in the sampled region. The experimental values of  $A$  against temperature were then curve fitted by linear regression analysis. Obtaining  $Q$  allows an absolute determination of surface concentration which does not depend on the assumption that bulk concentration is reflected in the surface layer following sputtering (ref. 3). Once  $Q$  is known,  $C_d$  as a function of  $T$  can be determined. With this calibration, both sputtering yield and possibly Auger yield can be determined.

## Effect of Sputtering

In order to investigate the effects of sputtering, a simple analysis can be performed. The rate of change of surface concentration can be obtained from the following equations by assuming sputtering is simply a surface process:

$$\left. \begin{aligned} \frac{dn_1}{dt} &= -k_1 n_1 + x_1 (k_1 n_1 + k_2 n_2) \\ \frac{dn_2}{dt} &= -k_2 n_2 + x_2 (k_1 n_1 + k_2 n_2) \end{aligned} \right\} \quad (3)$$

where

$n_1, n_2$  surface concentrations at time  $t$

$t$  time

$k_1, k_2$  sputtering rates of species 1 and 2, respectively, equal to  $yI$

$y$  sputtering yield

$I$  incident ion flux

$x_1, x_2$  fractional bulk concentration of species 1 and 2, respectively

The first terms in equations (3) represent the rate of sputtering of the species from the surface. The second terms represent the rate of exposure of species 1 and 2 at the surface as a result of sputtering. At steady state

$$\frac{dn_1}{dt} = \frac{dn_2}{dt} = 0$$

and the result is

$$\left. \begin{aligned} k_1 n_1 &= x_1 k_1 n_1 + x_2 k_2 n_2 \\ k_2 n_2 &= x_2 k_2 n_2 + x_1 k_1 n_1 \end{aligned} \right\} \quad (4)$$

Noting that  $x_1 + x_2 = 1$  gives

$$\frac{n_2}{n_1} = \frac{x_2}{x_1} \frac{k_2}{k_1} = \frac{x_2}{x_1} \frac{y_1}{y_2} \quad (5)$$

Therefore, from a knowledge of sputtering yields and bulk concentrations the ratio of steady-state surface concentrations can be obtained. This can be interpreted in terms

of fractional concentrations by assuming that the total number of atoms  $N$  in a surface plane is conserved:

$$n_1 + n_2 = N \quad (6)$$

Therefore,

$$1 + \frac{C_2}{C_1} \frac{y_1}{y_2} n_1 = N$$

and

$$\frac{n_1}{N} = \frac{1}{1 + \frac{C_2}{C_1} \frac{y_1}{y_2}} \quad (7)$$

### Evaporation

In order to estimate the amount of aluminum that would be removed by evaporation, the following relation is used (ref. 6):

$$\mu = 3.513 \times 10^{22} \frac{P}{(MT)^{1/2}} \quad (8)$$

where

- $\mu$       evaporation rate, atoms/(cm<sup>2</sup>)(sec)
- $P$       vapor pressure of aluminum at temperature  $T$
- $M$       atomic weight, g-atoms
- $T$       surface temperature

## RESULTS AND DISCUSSION

Figure 2 contains the raw data of the ratio of Auger peak-to-peak height at a temperature  $T$  to the peak-to-peak height at 793 K plotted against temperature. Figure 3 shows the results of the curve fit for  $C_1 = 0.1$  (ref. 3). The curve fit yields a value for  $Q$  from which surface concentration can be calculated. The experimental scatter for the calibration point of 793 K was  $\pm 1.5$  percent. As can be seen, equation (1) gives excellent fit for the data over the part of the curve from 523 to 843 K. At the low-temperature end of the curve, a phenomenon described by McClean (ref. 5) as "freezing in" occurs; that is, the diffusion coefficient becomes so low that equilibrium cannot be reached in the experimental time allotted. At the high-temperature end of the curve the more rapid decrease of aluminum probably results from the onset of evaporation.

The value of  $Q$  obtained from these results was 5780 joules per mole (1380 cal/mole). This is higher than the values reported in reference 3. The higher value is not surprising, however, since in that article the "freezing in" temperature was implicitly assumed to be room temperature. In this report the "freezing-in" temperature is approximately 523 K. The experimental spread in the present data is much smaller than that in reference 3. The surface concentration was completely reversible as a function of temperature; that is, the same results are obtained by starting at either low or high temperature.

It is interesting to examine the evaporation rate of aluminum at the calibration temperature of 793 K. With the use of equation (8) and an expression for the vapor pressure obtained from reference 6,

$$\mu = 1.05 \times 10^9 \text{ atoms}/(\text{cm}^2)(\text{sec})$$

Using the number density for a copper (111) plane implies that 0.1 percent of the atoms should leave during the experimental observation time of 30 minutes. This number is pessimistic in that individual vapor pressures should be lower in binary alloys (ref. 6).

Evaporation can be eliminated as a reason for the changes observed in aluminum peak height (fig. 2). The attempts to deposit aluminum on a tantalum sheet by heating the alloy at 793 K for 17 hours indicated an amount of aluminum deposited of approximately 0.5 percent of the change observed on the alloy surface. At 873 K and above, both copper and aluminum were deposited during the 17-hour heating; however, again the amount deposited on the tantalum represented a small percentage of the peak height change obtained looking directly at the crystal.

In reference 3 the assumption was made that, following the sputtering, the aluminum peak height represented bulk concentration in order to establish a calibration



technique. Although this may be a reasonable assumption for solid solutions, the field of sputtering of alloys is still not well established (ref. 7). In cases of some polycrystalline alloys, it has been observed that the yields of each constituent reflect the yields in the pure materials. Equation (7) predicts the steady-state surface concentration of each constituent resulting from sputtering. Using equation (7),  $y_1 = 2.3$ , and  $y_2 = 1.3$  (ref. 8) for 400 electron volt argon ions results in  $n_1/N = 0.152$ . Therefore, on the basis of pure metal sputtering yields, the ratio of aluminum to the total number of atoms in the surface would be 0.15 rather than the 0.1 used in reference 3. This says that in reference 3 the number of surface atoms could have been at worst underestimated. The present results, which are independent of sputtering, give essentially the same value of the ratio of maximum surface to bulk concentration ( $C_d/C_o = 3$ ) as the sputtering calibration in reference 1 ( $C_d/C_o = 3.1$ ). Therefore, it appears that the assumption of bulk concentration after sputtering is quite good. This indicates, then, that with this single-crystal solid solution, a single sputtering yield may be obtained rather than two independent ones. The value obtained also agrees with the interpretation of the LEED pattern obtained for this alloy in reference 3.

The final problem involved with the surface segregation measurement is the number of layers sampled with AES. In order to get quantitative results from Auger spectroscopy, it is necessary to estimate the depth of the target sampled (ref. 3). The present technique does not answer this question, unfortunately. Figure 4 shows the same raw data fit with the assumption that the surface layer and two bulk layers rather than one are sampled. As can be seen, the fit is still good. This curve fitting procedure is basically a two-parameter method, the number of layers sampled  $C_1$  and  $Q$ . Apparently with this many degrees of freedom and the basic equation, data of the type obtained in this study can be fit over a fairly wide range. Therefore, it is still necessary to base the present assumptions for the volume sampled on the physical reasons given in reference 3. A second difficulty exists with the present curve-fitting technique in that it is doubled valued. It also has a root for  $Q$  between 20 930 and 41 860 joules per mole (5000 and 10 000 cal/mole). However, this root implies  $C_d/C_o \sim 10$ , which is in disagreement with any possible interpretation of the number of layers sampled by AES (ref. 3).

## CONCLUDING REMARKS

A new technique for examining equilibrium surface segregation has been developed that is based on AES analysis at elevated temperatures. The method verifies equilibrium surface segregation by demonstrating reversibility of surface concentration with temperature. This result fits the trends predicted by McClean's analysis (ref. 3) and provides an absolute calibration for surface concentration for the copper-aluminum

alloy studied. From a physical standpoint it provides an interesting method for studying two-energy-level systems. The retrieval energy determined by this method could be used to predict surface composition for practical fields such as friction and wear where it is of paramount importance. The technique could also be used for obtaining information concerning total cross sections in AES and yields in sputtering of alloys.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, January 27, 1972,  
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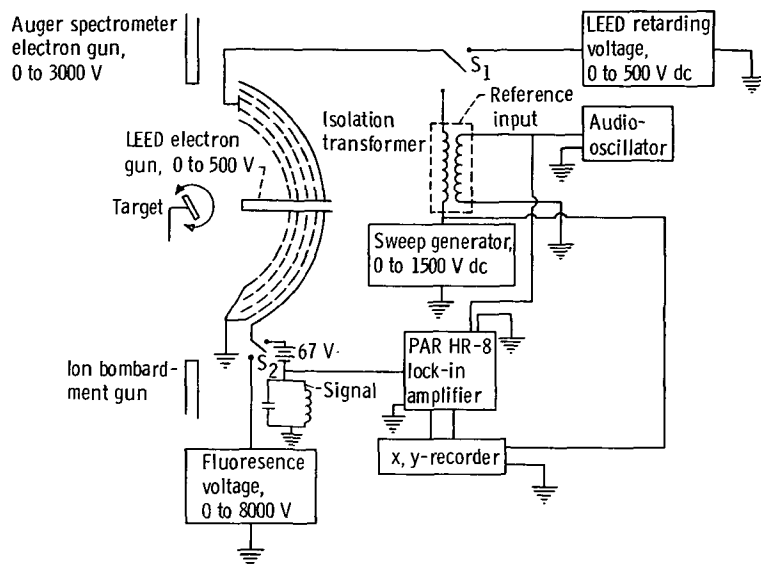


Figure 1. - Experimental apparatus.

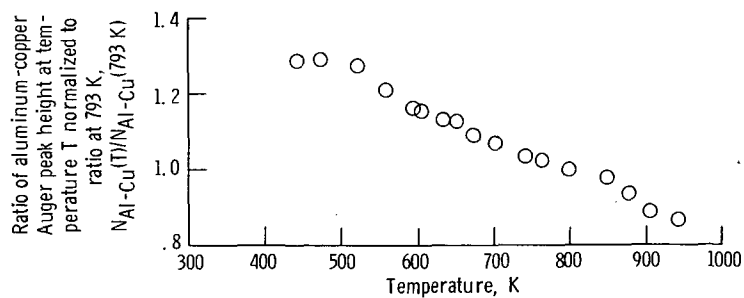


Figure 2. - Ratio of aluminum-copper Auger peak height at temperature T normalized to ratio at 793 K as function of temperature.

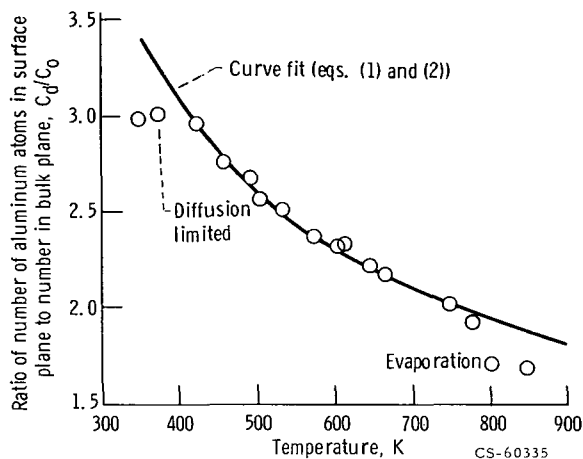


Figure 3. - Curve fit (eqs. (1) and (2)) giving ratio of number of aluminum atoms in surface plane to number in bulk plane as function of temperature. Sum of concentrations added for layers assumed sampled below surface layer  $C_1$ , 0.1; retrieval energy  $Q$ , 5780 joules per mole (1380 cal/mole).

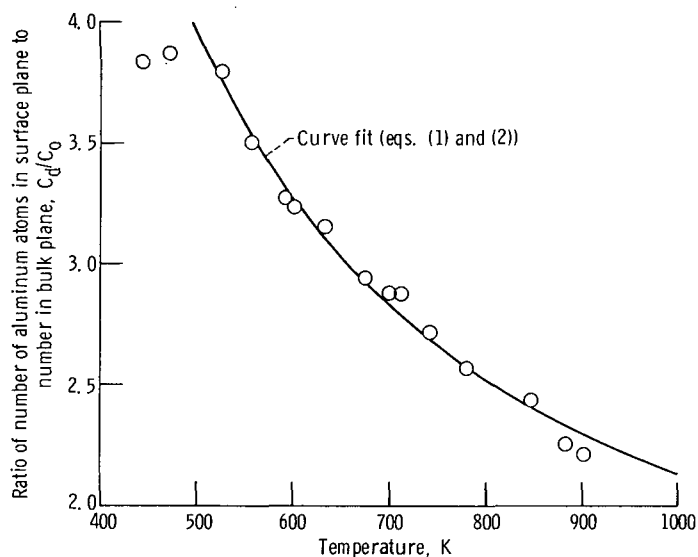


Figure 4. - Curve fit (eqs. (1) and (2)) giving ratio of number of aluminum atoms in surface plane to number in bulk plane as function of temperature. Sum of concentrations added for layers assumed sampled below surface layer  $C_1$ , 0.2; retrieval energy  $Q$ , 5780 joules per mole (1770 cal/mole).



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